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High-field ground-state level crossing and magnetic susceptibility of an $\{Fe_8\}$-cubane cluster

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The differential susceptibility, dM/dH, of an $\{Fe_8\}$-cubane cluster has been measured for magnetic fields up to 54 T at 1.3 and 4.2 K using a pulsed-field technique. The data feature a single strong peak at 42 ± 1 T, corresponding to a ground state level crossing at that field, in excellent agreement with the predicted value, 41 ± 1 T, obtained using a Heisenberg model of the cluster. The theoretical model also accurately accounts for detailed features of the temperature and field dependence of the width and height of the observed peak.

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I. INTRODUCTION

Due to swift progress[1–7] in the chemical synthesis of a wide variety of bulk crystalline samples of transition-metal cluster compounds, one can now explore the magnetic properties of diverse nanosize units. The dominant magnetic interactions within the bulk sample are intracluster interactions so that the sample is equivalent to a macroscopic ensemble of magnetically independent identical paramagnetic clusters. For one such recent cluster compound,[8] $\{Fe_8\}$ cubane, the subject of this Brief Report, it has been proposed[9] that the paramagnetic properties are due to two distinct intracluster isotropic exchange interactions between eight Fe^{III} ions (spin 5/2). The values of the two exchange constants were determined[9] by optimizing the fit between experimental and model data for the temperature-dependent weak-field magnetic susceptibility. However, a decisive confirmation of the model requires similar successes for other measurable quantities.

In this Brief Report we show that the theoretical model of Ref. 9 also correctly describes the magnetic field dependence of the differential susceptibility dM/dH at fixed low temperatures. In particular, we report results for this quantity using a pulsed-field technique up to 54 T for two temperatures, 1.3 and 4.2 K. Of special interest, our measured data exhibit a single well isolated peak at approximately 42 T. This is to be compared to the theoretical prediction of a single peak in this field range at 41 T. The model also provides a very simple quantitative explanation of the single peak in dM/dH. The peak is a direct consequence of the fact that the ground-state energy level has total angular momentum quantum number $S=0$ in the field range from 0 to 41 T, $S=1$ from 41 until 81 T,[10] followed by a transition to $S=2$, etc. Besides correctly reproducing the magnetic field associated with the peak, detailed features of dM/dH, in particular, the dependence of the width and height of the peak on H and T, are very well reproduced by the model, as shown below.

II. EXPERIMENT

The magnetization was measured on a powder sample at the Institute for Solid State Physics by a standard inductive method for asymmetric half-cycle sweeps with a duration of 10 ms. Utilizing fast digitizers, the inductive method provides data for dM/dt and dH/dt, which are subsequently integrated to give results for M versus H up to 54 T. The sample was immersed in liquid ^{4}He to maintain good thermal contact with the thermal bath. The resulting data for M versus H as obtained for the up and down portions of the half cycle were in good agreement, indicating that hysteresis effects are negligible. The measurements were performed for two temperatures, 4.2 K and 1.3 K. The data for dM/dH for 4.2 K are shown in Fig. 1, where a peak is clearly visible at $H\approx42$ T.

The peak that has been observed at 42 T is to be expected, as it corresponds to a zero-field energy gap of $\Delta/k_B \approx 55$ K between the $S=0$ (singlet) ground state and the $S=1$ (triplet) first excited state. (Here k_B denotes Boltzmann's constant.) This value of Δ was previously reported in Ref. 9. As the field increases from zero, the gap shrinks between the $S=1$, $M=1$ state and the $S=0$, $M=0$ state, until these energy levels cross. The expected level-crossing field, H_1, is given by the relation $g\mu_B H_1=\Delta$, where the spectroscopic splitting factor is chosen as $g=2$, yielding $H_1=41$ T. The small discrepancy between the values of the predicted (41 T) and observed (42 T) level-crossing fields can be attributed to the small uncertainty in the model parameters that were determined in Ref. 9.

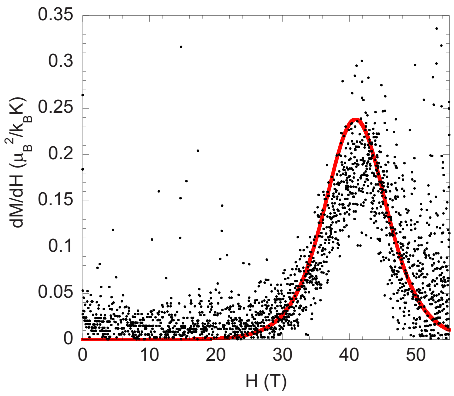

FIG. 1. (Color online) Differential susceptibility per cluster, dM/dH, versus field, H, for $T=4.2$ K, showing experiment (symbols) and theory (solid curve).

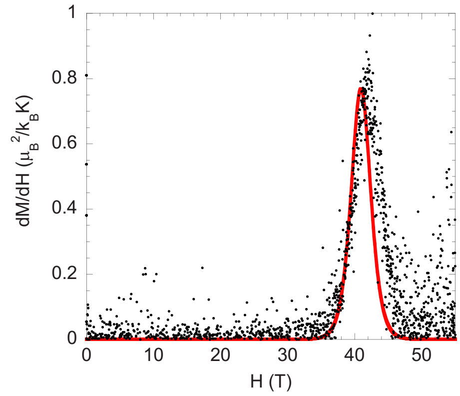

FIG. 2. (Color online) Differential susceptibility per cluster, dM/dH, versus field, H, for $T=1.3$ K, showing experiment (symbols) and theory (solid curve).

A detailed theoretical description of the present data can be achieved using a simplified (two-level) replacement of the Heisenberg model. This is because—although the full energy spectrum of $\{Fe_8\}$ cubane involves more than 10^6 eigenstates—for $H<54$ T only the state $S=1$, $M=1$ has an energy within 50 K of the $S=0$, $M=0$ ground state. Hence, for $T<5$ K, only these two states will have a significant thermal occupation. Therefore, we are able to use a two-level model, for which dM/dH is given by

$$\frac{dM}{dH}=\frac{1}{4}(g\mu_B)^2\beta\,\mathrm{sech}^2(y), \tag{1}$$

where M denotes the magnetic moment of an individual cluster, $\beta=1/k_BT$, and $y=\beta(g\mu_BH-\Delta)$. The solid line that appears in Fig. 1 is given by Eq. (1) upon setting $g=2$ and $\Delta/k_B=55$ K. Due to the nature of the experiment, the measured values of dM/dH were initially expressed in arbitrary units. To obtain the absolute units shown in Fig. 1, the experimental data were multiplied by a constant factor, $0.23\mu_B^2/k_B$ K, in order to optimize the fit between theory and experiment.[11] This process of fitting the $T=4.2$ K data to Eq. (1) fixed the value of the only adjustable parameter. It should be noted that the width of the measured peak is in excellent agreement, irrespective of this calibration process. To verify the applicability of the two-level formula of Eq. (1), the measurement was repeated at $T=1.3$ K, and these data were multiplied by the same constant, $0.23\mu_B^2/k_B$ K. This lower temperature measurement should yield a narrower, taller peak in dM/dH, still occurring at the same field. These data are shown in Fig. 2, where indeed the peak has become narrower and taller. These measurements are in very good agreement with the theory, where the solid line in Fig. 2 is given by Eq. (1), again setting $g=2$ and $\Delta/k_B=55$ K.

III. DISCUSSION

The key result of this Brief Report is that our measurements of the differential susceptibility dM/dH of the $\{Fe_8\}$-cubane cluster are in quantitative agreement with the predictions based on the Heisenberg model proposed in Ref. 9. In particular, we have observed a ground-state level crossing at 42 T, in close agreement with the predicted (41 T) field value. Moreover, the temperature and field dependence of the corresponding peak in dM/dH are in close agreement with that predicted by the model. Alternatively, the present measurements could have shown this model to be insufficient for describing the present data since the parameters of the Heisenberg model, namely, the values of the exchange constants, were determined[9] solely by optimizing the fit between the experimental and theoretical temperature-dependent weak-field susceptibilities. It is therefore both satisfying, and quite remarkable, that this cluster can be so successfully described by a simple isotropic Heisenberg model based on two exchange constants.

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[10] The existence of a second predicted level crossing at 81 T is due to the fact that in zero field the next higher level has $S=2$ with an energy 164 K above the lowest $S=0$ level (Ref. 9). This could not be tested, as it is outside the current range of our experimental facilities.

[11] The measured magnetization versus field was independently calibrated using a standard sample, and it was found that the value of the magnetization at 55 T and 1.3 K was indeed $2\mu_B/\mathrm{f.u.}$, in agreement with theory.